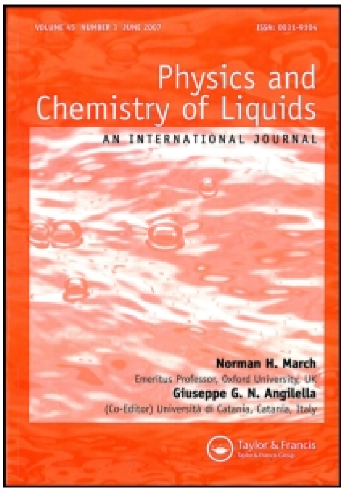

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VISCOSITY OF BROMOALKANES: CALCULATIONS ON THE BASE OF STRUCTURAL AND CONFORMATIONAL CHARACTERISTICS OF MOLECULES

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The equation, taking into account the conformational molecular characteristics, is used for the calculation of the viscosity of bromoalkanes. It is shown that the viscosity of the compounds under investigation can be described adequately by means of this equation.

KEY WORDS: Viscosity, molecular conformations, organic liquids, bromoalkanes.

1 INTRODUCTION

In accordance with current concepts, the liquid viscosity is conditioned basically by the two factors, depending on the transfer of momentum as a result of intermolecular collisions and of intra-molecular forces, also. This fact caused the development of the number of empirical approaches to the viscosity calculations, based on the additive schemes. Underlying for these methods is the use of atomic and molecular constants, every method being oriented on the definite structural class of molecules and on the definite interval of temperatures. The computational errors are usually great. In this connection it seemed important from the theoretical and practical points of view to devise a simple analytic expression which relates the liquid viscosity η and the structural (including conformational) characteristics of the molecules.

2 THEORY

The following equation received in the work[1] describes viscosity η of the organic liquids on the base of the structural and conformational features of molecules:

$$\eta = (1 - \theta \ln N_c)^{-1} \left(\sum_{i,j}^{S} \mu_{ij} n_i n_j \right) (d/M)^{2/3}. \qquad (1)$$

In the Eqn. (1) d and M are respectively density (kg/m^3) and molecular mass (kg/mole) of the liquid under consideration: n_i and n_j are the numbers of atoms entering in the molecular structure of the molecule of the liquid and belonging to the i-th and and j-th sorts. In the process of flow these atoms take part in passing of the moment of motion quantity μ_{ij} (N·s) due to the bimolecular collisions in the liquid phase along the axis, which is parallel to the liquid's flow direction. S (see Eqn. (1)) is the total number of atom's sorts in the molecule which are capable of participation in the intermolecular impulse transfer (μ_{ij}) with the account of molecular stereochemistry. Further, N_c is the number of energetically degenerated (or quasi-degenerated) conformational states of the one separate molecule; states, among which the conformational transitions in the current liquid phase by the definite temperature T and pressure P are realized. Undimensional quantity θ in (1) which is constant for any liquid if T and P are constant can be presented (see[1]) as:

$$0 < \theta = (\ln N_{\mathrm{cr}})^{-1} < 1 \qquad (2)$$

where N_{cr} is some critical number of conformational states possible for the molecular systems under consideration while T and P are given.

As it was shown[1], the first multiplier in the Eqn. (1) designated below as a function $G(N_c)$ describes intermolecular collision probability's increase due to conformational transitions; then the presence of θ in the factor is conditioned by the following property of the function $G(N_c)$: $G(N_c) \to \infty$ when $N_c \to N_{\mathrm{cr}}$. The latter results from the presence of the transition from liquid homologues to solid ones (i.e. the transition from finite values of η to $\eta \to \infty$) in different homological series of the organic compounds. The number N_c in the Eqn. (1) is supposed to be equal to the total number of local minimums on the surface of full potential energy of the molecule, arising in the latter under all possible internal rotations, which change the conformation of its non-hydrogen skeleton. The non-hydrogen atoms are considered here nonequivalent, so that conformations similar to the two nonpolanar conformations of n-butane are different. Rotation of the end-groups (methyl-typed) don't cause N_c's increase. Having this in mind, we can easily find that N_c, for example, is equal to 1 for propane and isobutane, to 3^2 for pentane, to 3^3 for hexane and to 3^{n-3} for every normal alkane (n-C_nH_{2n+2}). Therefore, the Eqn. (1) takes for the normal paraffin the following form:

$$\eta = [1 - \theta(n-3)\ln 3]^{-1} 4\mu_{\mathrm{HH}}(n+1)^2 (d/M)^{2/3}. \qquad (3)$$

In (3) we don't take into consideration those collisions, in which sp^3-hybrid carbon atoms take part, screened sterically by hydrogen ones.

In the work[1] it was shown for normal paraffin from pentane to tridecane that when $T = 293.15$ K, $P = 1.01325 \times 10^5$ Pa and also when $\theta = 0.05681$ ($N_{\mathrm{cr}} = 3^{16}$) and $\mu_{\mathrm{HH}} = 3.454 \times 10^{-7}$ N·s then the Eqn. (3) describes viscosity of the compounds listed properly. Besides for the series of n-alkanes, the values η were calculated also for the organic compounds belonging to the such structural classes as 1-alkanes, alkylbenzenes, simple and complex ethers with the use of the corresponding values of μ_{ij} in the Eqn. (1)[1]. This enabled to show not only constancy of μ_{ij} for the structural class

Table 1 The results of calculating bromoalkanes viscosity on the base of Eqn. (1).

Ns.	*Compound:*	*M* *(kg/mole)*	N_c	*d(kg/m³)*	$\eta \times 10^3 (Pa \cdot s)$	
					calcul.	*exper.*
1	1-Bromopropane	123.00	3	1354	0.469	0.525[a]
2	1-Bromobutane	137.02	3^2	1276	0.646	0.631
3	1-Bromopentane	151.06	3^3	1218	0.839	0.794
4	1-Bromohexane	165.08	3^4	1176	1.056	0.977
5	1-Bromoheptane	179.11	3^5	1140	1.30	1.26
6	1-Bromooctane	193.13	3^6	1118	1.603	1.622
7	1-Bromononane	207.15	3^7	1084	1.947	1.995
8	1-Bromodecane	221.17	3^8	1051	2.367	2.344
9	1,1,2,2-Tetra-bromoethane	345.67	1	2967	9.886	9.797

[a]experimental values of η for bromoalkanes were taken from[3,4].

of compounds given, but also the applicability of μ_{ij} (when T and P are chosen) for the calculation of η when the compounds taken differ in their structure.

3 RESULTS AND DISCUSSION

In the present paper applicability fo the Eqn. (1) to the compounds of new structural class, bromoalkanes, is considered. In Table 1 the results of calculating bromoalkanes viscosity on the base of the Eqn. (1) are presented. To calculate η for bromoalkanes the values d needed were taken from[2]. When calculating viscosity of bromoalkanes ($T = 293.15\,\mathrm{K}$ and $P = 1.01325 \times 10^5\,\mathrm{Pa}$) the following μ_{ij} were used side by side with μ_{HH} and θ: μ_{HBr}, μ_{CBr}, and μ_{BrBr} being equal respectively to -96.64×10^{-6}, 221.14×10^{-6}, and 85.05×10^{-6} N·s. Taking into consideration that in the atom of bromine there are unshared electron pairs on 4p-atomic orbitals possessing considerable spacial extent, the atom-atomic interactions of the bromine–carbon type were taken into account. Below the usual notation for the Eqn. (1), which arise when calculating viscosity of compounds in view is represented for 1-bromopropane as an example.

$$\eta_{C_3H_7Br} = (1 - \theta \ln N_c)^{-1}(7^2\mu_{HH} + 7\mu_{HBr} + 3\mu_{CBr} + 1^2\mu_{BrBr})(d/M)^{2/3}. \qquad (4)$$

4 CONCLUSION

It is important to note that the possibility to calculate μ_{ij} on the base of some characteristics (for example, atomic weights) of the atoms, taking part in some definite type of atom-atomic collisions is an important theoretical and practical task, associated with the use of the Eqn. (1). It may be solved evidently only after the values μ_{ij} corresponding to the various types of atom-atomic collisions are known in the process of practical use of the Eqn. (1) (T being constant).

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